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Study of Optical Properties of Co-evaporated PbSe Thin Films

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ABSTRACT

Thin films of Lead Selenide (PbSe) of thicknesses ranging from 1050 Å to 5500 Å have been prepared by co-evaporation technique, onto precleaned amorphous glass substrates. The deposited samples were annealed and annealed samples were used for characterization. The XRD analysis confirms that lead selenide films are polycrystalline having cubic structure. The lattice parameters of thin films are almost matching with ASTM data for lead selenide. The transmittance and reflectance have been measured at normal incidence in the spectral range (200-2600 nm). The dependence of adsorption coefficient, on photon energy have been determined. Analysis of result showed that for co-evaporated PbSe films of different thicknesses direct transition occurs with band gap energies in the range 1.08 eV to 1.54 eV. Refractive indices and extinction coefficients have been evaluated in the above spectral range.

Keywords: X-ray diffraction, Optical properties, Band gap, Refractive indices.

INTRODUCTION

Lead chalcogenides (IV-VI) are proved to be promising materials, because of their uses as IR detector, photographic plated, selective and photovoltaic absorbers and lasers [1-6] etc. Multilayer IV-VI compound semiconductors have recently attracted considerable interest because of their structural, electrical and optical properties. Literature review indicates that the most of the studies of quantum size effect were concentrated in (II-IV) and to much lesser extent oxide semiconductors of the remaining semiconductors. PbS has been the most investigated. Relative few studies have been reported on the lead selenide [7-12] in addition to these some evidences was recently reported for the presence of an amorphous PbSe phase in polycrystalline films of PbSe prepared by chemical deposition [13]. Therefore in this work systematic investigation of the effect of preparation conditions on the structural characteristics and optical properties has been carried out. An interpretation of the determined optical constants variations in correlation with the corresponding structural parameter is presented.

MATERIALS AND METHODS

Polycrystalline PbSe co-evaporated films have been deposited via sublimation of the two basic ingredients by three-temperature technique, under vacuum about 10^{-5} torr. The deposition was controlled by adjusting the rate of both sources of sublimations. The substrates to source distance have 20 cm. The glass substrates were cleaned with warm dilute chromic acid, detergent solution, distilled water and acetone in that order. The samples of different thicknesses (1050 Å, 1370 Å, 1530 Å, 2310 Å, 2650 Å, 5490 Å) at constant substrate temperature (373 K) were deposited under similar conditions. The deposition rate was maintained 20-40 Å/sec throughout sample preparations. The films were annealed at reduced pressure 10^{-5} torr and at temperature 523 K for the period of three hours. The thicknesses of films were controlled by using quartz crystal thickness monitor model No.DTM-101 provided by Hind-High Vac. These samples were then used for various characterizations.

The X-ray diffractograms (Rigaku, Miniflex Japan) were obtained of these samples to obtain the structural information and to identify the film structure qualitatively. The scanning angle (2θ) range was from 20° to 80°(CuKαline). The X-ray shows that all the films prepared were polycrystalline with cubic structure. Scanning electron microscopy (SEM) was performed using model 501, Philips, Holland with EDAX attachment. A double beam spectrophotometer, Hitachi – 330 Japan, was used for optical studies in the wavelength range of 200 – 2600 nm. The absorption coefficients, type of transition, optical constants and optical band gap were determined from these studies for all the co-evaporated thin films.

RESULTS AND DISCUSSION

The structural properties have been studied by X-ray diffractogram Cukα radiation 1.5418 Å for annealed samples of thicknesses 1530 Å, 2310 Å, 2650 Å, and 5490 Å are presented in Fig.-1. All XRD's of PbSe films of different thicknesses are identical in nature with slightly different in peak intensity. From a diffractogram, it is also found that the number of reflection increases with thickness of sample. It also indicates that growths of films are in preferred orientation along [200] direction and these films clearly shows that PbSe films are of well defined polycrystalline in nature. The observed diffraction data is compared with standard (ASTM file No 6-354) in Table No-1. The observed data of all samples of various thicknesses very closely match with standard values, confirming PbSe films are of cubic system with a lattice parameter a_o = 6.126 Å. From X-ray diffractogram of thickness 2650 Å, it is seen that a pair of peaks followed by single peak, which is again followed by a pair of peaks and another single peak.

Table 1. Comparison of standard observed XRD data

Standard					Observed	
d Value	Intensity	h	k	l	d Value	Intensity
3.06	100	2	0	0	2.9375	100
2.165	70	2	2	0	2.1028	38
1.846	18	3	1	1	1.8090	21
1.768	20	2	2	2	1.7523	18
1.531	14	4	0	0	1.5007	22
1.369	25	4	2	0	1.3396	31
1.250	16	4	2	2	1.2341	20

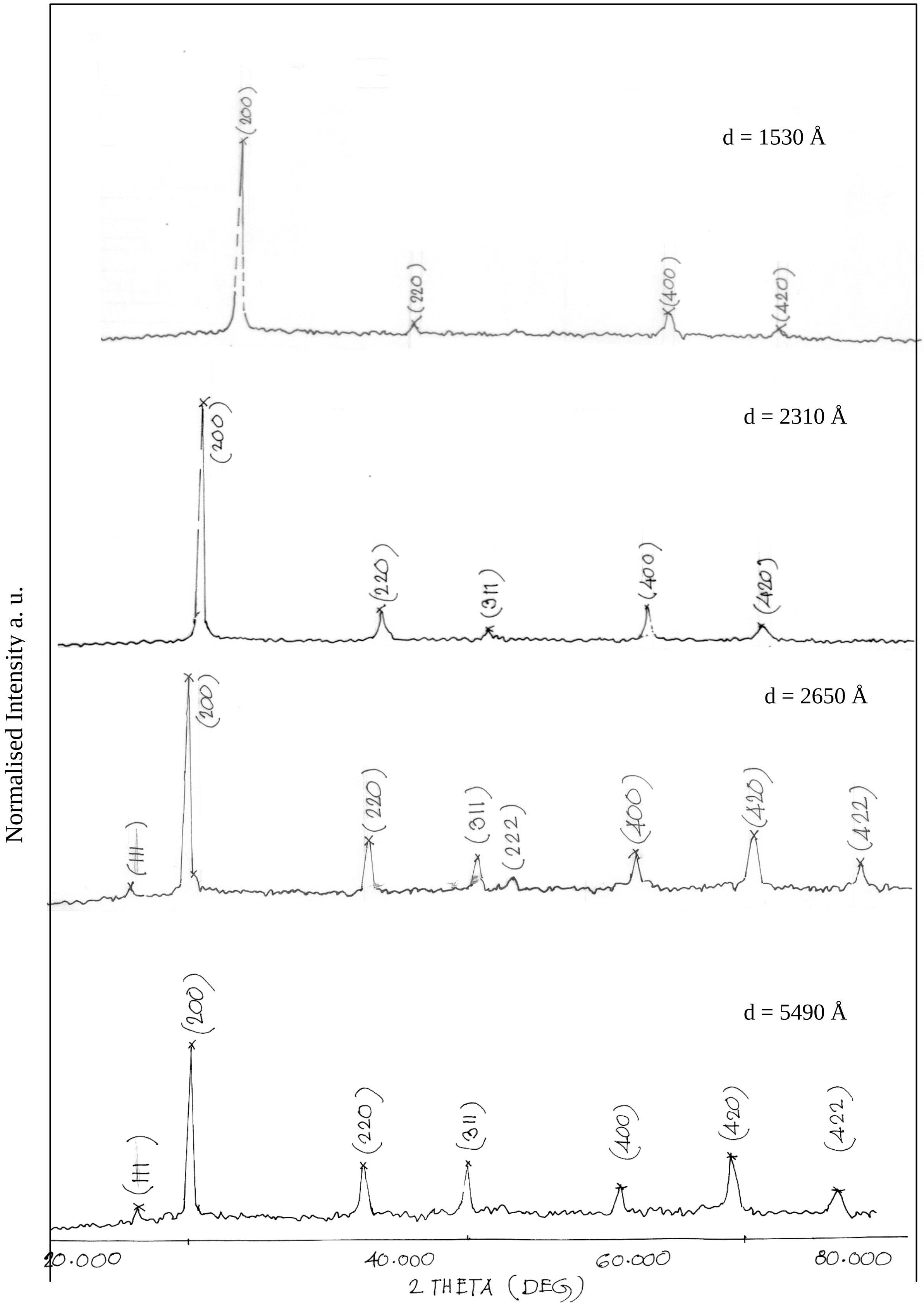

Fig.1 X-ray diffractograms of various thicknesses of PbSe thin films.

This is a typical characteristic observation of a face centered cubic (fcc) structure [14] In the present work the observed diffraction parameters closely agree with standard value taken from PbSe card (6-354) confirming that the bulk alloys and co-evaporated thin films are of near stoichiometric PbSe.

Diffraction analysis indicates that PbSe films are polycrystalline and grain sizes are determined by using Schrerres formula [15],

$$Cs = \frac{K\lambda}{B\cos\theta} \qquad (1)$$

Where K is a shape factor usually $\cong 1$, λ is the wavelength of the X-ray (1.5418 Å), θ is the Bragg's angle and 'B' is the corrected FWHM. The range of crystallite size estimated for annealing film samples was from 117 to 282 Å.

Scanning electron micrograph (SEM) of lead selenide thin film of thickness 2310 Å is presented in Fig.-2. Deposited PbSe films are light gray in colour with good adhesion for the substrate. The morphology of such film shows that it is polycrystalline with crystallites randomly scattered on the surface aggregates of crystallites are visualized on the surface.

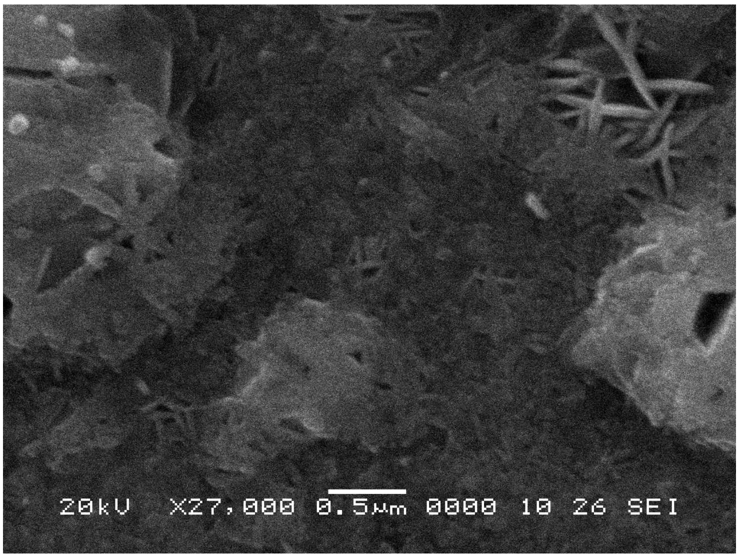

Fig. 2 Scanning Electron Micrograph of PbSe thin film (d = 2310 Å)

EDAX analysis gave up the mass percentage 20.52 and 79.48 for Se and Pb elements. It has ideally theoretical mass percentage 27.84 and 72.16 respectively. It has ideally theoretically 50:50 %. This indicates the deviation of stoichiometry of PbSe in film material.

Optical Properties

The reflectance and transmittance spectra of these samples were recorded using Hitachi spectrophotometer model – 330 in the spectral region 200 – 2600 nm. Using these data, the absorption coefficient 'α' has been calculated by applying the relation,

$$\alpha = \frac{2.303}{d}\ln(1/T) \qquad (2)$$

The absorption coefficient can be written in general form as a function of incident photon energy hν as Panakove[16],

$$\alpha h\nu = A_0 (h\nu - Eg)^{p} \qquad (3)$$

Where, p has discrete values like 1/2, 3/2, 2 or more depending on whether the transition is direct or indirect and allowed or forbidden. In the direct and allowed cases P=½ where as for the direct but forbidden cases it is 3/2. But for the indirect and allowed case P=2 and for the forbidden cases it will be 3 or more. And the constant A_o is given by

$$A_0 = [e^2/neh^2 m_e^*] (2m_r)^{3/2} \qquad (4)$$

Where m_e^* and m_r are the effective and reduced masses of charges carriers respectively. Eg is the optical band gap, the value of 'P' determined the nature of optical transition.. The results have been analyzed according to the relation (3).

Optical constants, refractive indices and extinction coefficients, have been evaluated from the reflection data and using the relations. Goawami [17]

$$R = \frac{(n-1)^2 + K^2}{(n+1)^2 + K^2} \qquad (5)$$

and

$$\alpha = \frac{4\pi\kappa}{\lambda} \qquad (6)$$

Absorption coefficients have been evaluated using percentage transmittance data as a function of wavelength presented in Fig.-3 for the samples of different thicknesses.

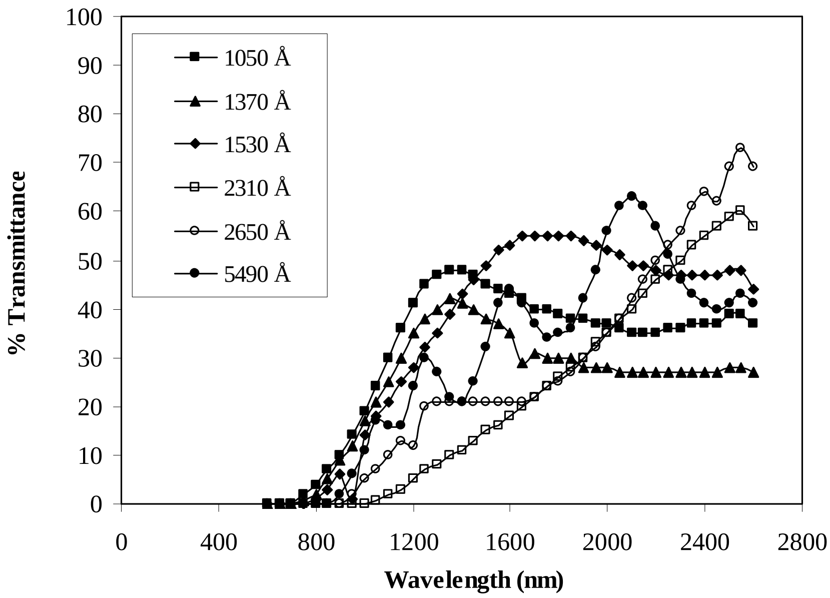

Figure 3. Spectral behaviour of transmittance with wavelength of PbSe thin films.

The optical transition observed by different worker is more or less in agreement with one another as for as the gap width of approximately 0.80 eV is concerned. The transmission data have been used to plot the curves of $(\alpha h\nu)^2$ Vs hν are presented in Fig.-4. These curves clearly show linearity and by extra polluting gives rise the direct transition band gap.

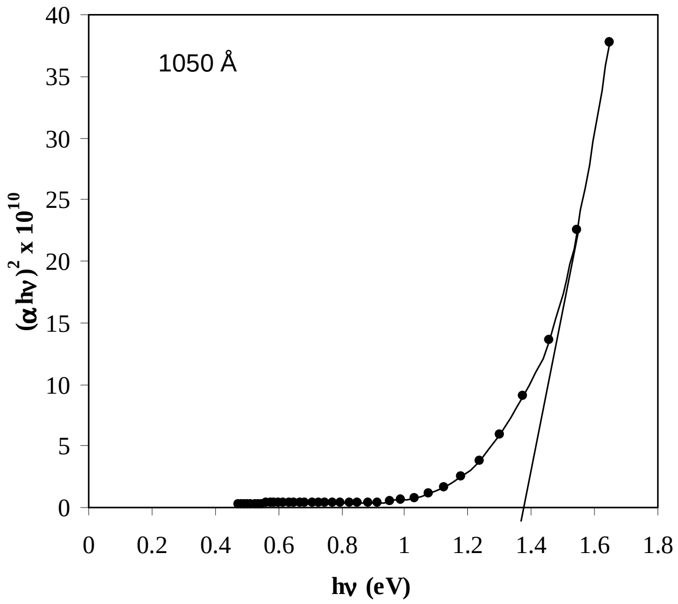

Figure 4. Variation of $(\alpha h\nu)^2$ with photon energy for PbSe.

It is seen that band gap is shifted as a function of thickness. The evaluated values of band gap energies are 1.54, 1.46, 1.37, 1.08, 1.18 and 1.23 eV for the samples of thicknesses 1050, 1370, 1530, 2310, 2650 and 5490 Å respectively. It is however difficult to account for the observed band gap shift as a function of thicknesses. The possible causes of observed band gap shift may account to one or more of the following mechanisms.

i) Presence of quantum size effect originated by the microstructure nature of the film with average grains sizes less than 300 Å [18-19].
ii) Defect induced adsorption caused by incomplete transformation of meta stable hexagonal for cubic phase [18].
iii) Change in stoichiometry due to loss of metal ion with that treatment which shifts the value of energy gap. Farrow and Jones [20]
iv) PbSe should show very low values of electron and hole effective masses (average electron, hole and reduced effective masses are 0.047, 0.041 and 0.022 respectively) for a crystalline size less than Bohrs diameter and increase in effective band gap due to size quantization and blue shifts in photoconductivity spectral response of evaporated PbTe and PbSe were attributed to small crystal size. Dalven [21]

Sascha Gorer [22] had studied quantum size effects in chemically deposited lead selenide films. They reported variation in band gap energies in the range from 0.55 to 1.55 eV and they showed that a wide range of different optical properties can be obtained with values of Eg ranging from 0.55 to 1.55 eV.

Also the estimation of grain size of PbSe films in the present work (200 – 400) Å which is well within nano-micro that is quite supports quantized effect of band gap energies in the range 0.50 to 1.55 eV.

Refractive index and extinction coefficient

The variation of refractive indices and extinction coefficients as a function of wavelength is presented in Fig.-5 and Fig.-6 respectively for the thicknesses 1050, 5490 Å. From these figures it is found that there is remarkable variations in 'n' and k as a function of wavelength and strongly depend on thickness of the sample. The variation in 'n' is no longer systematic as a function of thicknesses. Also these variations are quite distinguished in two wide wavelength regions namely (0.75-1.30)μ and (1.30-2.60)μ.

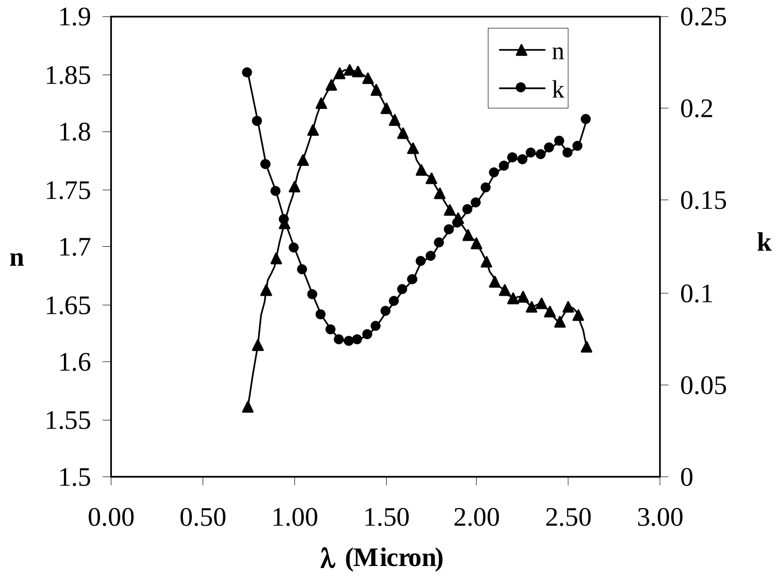

Figure 5. Variation of 'n' and 'k' with Wavelength

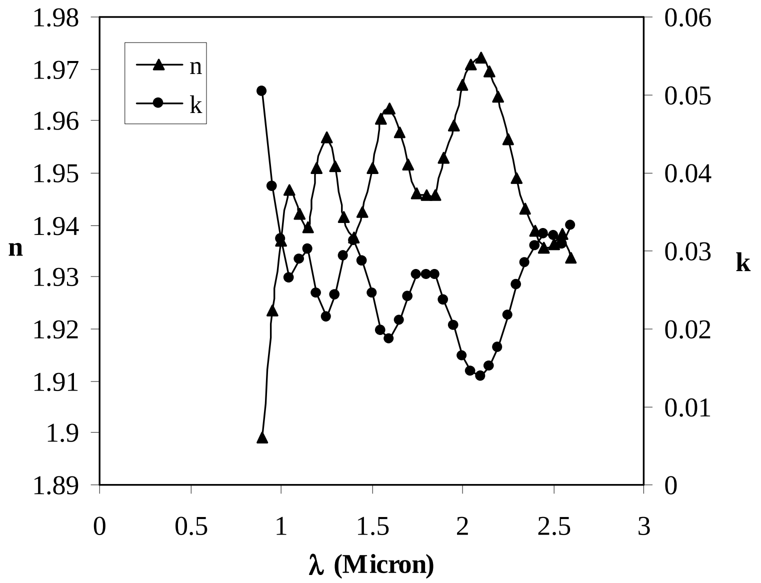

Figure 6. Variation of 'n' and 'k' with Wavelength

Refractive indices vary from 1.62 to 1.97 while the range of variation of extinction coefficient is from 0.013 to 0.227. This is presented in Table-2.

The observed variation in 'n' value is theoretically expected. Theoretically refractive indices increased with denser medium. For highly transparent non-absorbing medium 'n' is greater than '1'. In such case naturally reflectance is very low even less than 5-10 %. While reflectance is more than (50-60) percent 'n' values are high and when reflectance approaches to 100 % 'n' may be infinity.

Table 2. Optical parameters of PbSe thin films

d (Å)	Range of 'n'	Range of 'K'	λsp	'K' (Steep Maxima)
1050	1.85 – 1.56	0.073 – 0.219	0.75	0.219
1370	1.86 – 1.54	0.067 – 0.227	0.75	0.227
1530	1.89 – 1.62	0.050 – 0.189	0.80	0.189
2310	1.91 – 1.62	0.044 – 0.189	1.05	0.189
2650	1.95 – 1.76	0.023 – 0.118	0.95	0.118
5490	1.97 – 1.89	0.013 – 0.050	0.90	0.050

The range of wavelength at which transmittance is constant, increase with the thickness of the sample. The above equation (6) indicates that for a given sample if thickness is constant and if transmittance is constant, then 'K' is directly proportional to the function of wavelength λ and therefore the variation on 'K' as function of λ for specified conditions d = constant and T = constant should be linear straight line with slope = [2.303/ d log (1/T) 1/4π] which is constant. Table-2 presents K steep-max and corresponding λsp for different thicknesses. It is seen from this table that K steep-max is decreased with increasing thickness of film. It is observed that the number of maxima and minima depend upon the thickness of the film sample by Khairnar [23]. No such observations are reported earlier for co-evaporated PbSe material in thin film form as reviews of literature indicate.

CONCLUSION

Single-phase polycrystalline co-evaporated lead selenide thin films have been deposited on to amorphous glass substrates, as revealed from XRD analysis and evaluated crystallite size ranging from 117 Å to 282 Å only. The lead selenide thin films are stoichiometric in nature with cubic in structure. The dependence of optical parameters of the films on light energy supports the direct characters of the interband transition through an optical band gap in the range 1.08 to 1.54 eV that is thickness dependence. There is remarkable variations in optical constants as a function of wavelength and strongly depend on thickness of the sample. The variation in 'n' is no longer systematic as function of thickness.

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